A Search for Interstellar Pyrimidine

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ABSTRACT

We have searched three hot molecular cores for submillimeter emission from the nucleic acid building-block pyrimidine. We obtain upper limits to the total pyrimidine (beam-averaged) column densities towards Sgr B2(N), Orion KL and W51 e1/e2 of $1.7 \times 10^{14} \text{cm}^{-2}$, $2.4 \times 10^{14} \text{cm}^{-2}$ and $3.4 \times 10^{14} \text{cm}^{-2}$, respectively. The associated upper limits to the pyrimidine fractional abundances lie in the range $(0.3-3) \times 10^{-10}$. Implications of this result for interstellar organic chemistry, and for the prospects of detecting nitrogen heterocycles in general, are briefly discussed.

Key words: astrobiology – ISM: individual (Orion KL, Sgr B2(N), W51 e1/e2) – ISM: molecules – line: identification.

1 INTRODUCTION

Molecular clouds contain many organic molecules that are known to be important in biochemistry. Astronomical observations, particularly at radio wavelengths, allow us to determine the chemical composition and characteristics of this molecular inventory (e.g. Dickens et al. 2001; Charnley, Ehrenfreund & Kuan 2001). Following incorporation into protostellar disks and comets, these molecules, or their descendants, were probably the major source of volatile organic material available to the early Earth (Chyba et al. 1990). Studies of molecular cloud composition therefore enable us to quantitatively address the issue of the connection between interstellar chemistry, the organic composition of primitive Solar System material, and the origin, evolution and distribution of Life in the Galaxy (e.g. Ehrenfreund & Charnley 2000; Ehrenfreund et al. 2002).

Many organics that are known, or strongly suspected, to be present in interstellar clouds, are fundamental components of the large organic macromolecules that are central to biochemistry. Examples of these are sugars and amino acids, the respective building blocks of polysaccharides and proteins. The simplest of these, glycolaldehyde and glycine, are both identified in the interstellar medium (Hollis et al. 2000; Kuan et al. 2003a).

Until recently, definitive detections of interstellar

1981, 1982), and also may be components of Comet Halley's CHON dust (Krueger, Korth & Kissel 1991).

The molecular composition of hot molecular cores is known to largely reflect the solid state chemistry that occurred on grain surfaces, prior to their deposition into the gas after protostellar dust heating (see Ehrenfreund & Charnley 2000). Reactions between HCN

ring compounds have been scarce (e.g. ethylene oxide, Dickens et al. 1997) and previous searches for imidazole, cyanoform, pyrrole and pyrimidine were unsuccessful (Simon & Simon 1973: Myers, Thaddeus & Linke 1980; Irvine et al. 1981). Recently we have tentatively detected the azaheterocyclic compounds 2H-azirine (c-C₂H₃N) and aziridine (c-C₂H₅N) at mm wavelengths (Kuan et al. 2003b; Charnley, Ehrenfreund & Kuan 2001). Two (different) tentative lines of Aziridine have also been claimed by Dickens et al. (2001). These observations suggest that biochemically important ring molecules may await detection. Of these potential discoveries, a key interstellar molecule for Astrobiology, comparable in importance to glycine, would be pyrimidine (c- $C_4H_4N_2$), the unsubstituted ring analogue for three of the DNA and RNA bases: thymine, cytosine and uracil. Interstellar pyrimidine was unsuccessfully searched for at 46 GHz 30 years ago (Simon & Simon 1973). Evidence for various purines and pyrimidines in space, including pyrimidine, comes from the fact that they have been detected in meteoritic organic matter (Stoks & Schwartz 1981, 1982), and also may be components of Comet Hal-

and VyCN (CH₂CHCN) on the surface of dust grains has been suggested as a possible source of interstellar pyrimidine (Simon & Simon 1973). Observations of hot cores,

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Table 1. Source List

Source	R.A.(B1950)	Dec(B1950)	$V_{\rm LSR} \ ({\rm km~s^{-1}})$	
Orion KL	$05^h \ 32^m \ 47^s.00$	$-05^{\circ} 24^{'}30^{''}.0$ $-28^{\circ} 21^{'}15^{''}.0$ $+14^{\circ} 24^{'} 39^{''}.0$	8.0	
Sgr B2(N)	$17^h \ 44^m \ 10^s.20$		64.0	
W51 e1/e2	$19^h \ 21^m \ 26^s.30$		60.0	

known to contain other rings believed to have formed on dust prior to evaporation, such as $c\text{-}\mathrm{C}_2\mathrm{H}_4\mathrm{O}$ (ethylene oxide) (Dickens et al. 1997; Nummelin et al. 1998) and $c\text{-}\mathrm{C}_2\mathrm{H}_3\mathrm{N}$ (Charnley, Ehrenfreund & Kuan 2001), do show the very high abundances of the HCN and VyCN molecules required for formation of N-heterocycles (Ziurys & Turner 1986; Turner 1991; Nummelin & Bergman 1999). Alternatively, experiments indicate that energetic processing of ices (e.g. Allamandola, Bernstein & Sandford 1997) leads to an organic residue containing many polycyclic aromatic hydrocarbons (PAHs) (Greenberg et al. 2000). One may speculate that similar processing of interstellar ice analogues containing ammonia, molecular nitrogen, and hydrogen cyanide, may similarly produce N-heterocycles like pyrimidine.

Hence, searches of hot molecular cores, employing highquality spectroscopic data, may offer the best chance of a pyrimidine detection. In this paper we report the results of a search towards three massive star-forming regions for submillimeter emission from pyrimidine.

2 OBSERVATIONS

We carried out a program of submillimeter observations using the James Clerk Maxwell Telescope (JCMT)¹ on Mauna Kea, Hawaii during Semester 01B over the period September 9–13, 2001. Additional measurements were made on November 23, December 1–2, and December 10, 2001. Our target list is given in Table 1; Column 4 gives the nominal LSR velocity of each source adopted for the search. The source list consists of three well-studied regions of massive star formation which are known to be rich in complex organic molecules (e.g. Blake et al. 1987; Miao et al. 1995; Remijan et al. 2002).

The heterodyne receivers used were the dual-channel B3 SIS mixers in the single-sideband mode (SSB) for the 345 GHz submilliter band (315–373 GHz). The sideband rejection was \sim 13 dB (a factor of \sim 20). The SSB system temperatures in fair (medium) weather conditions – atmospheric opacity τ (225 GHz) between 0.08 and 0.12 – were generally \sim 400 to 550 K. At 329.9 and 363.1 GHz, however, $T_{\rm sys}$ as high as \sim 700 K and \sim 900 K were recorded, due to poor atmospheric transmission and higher receiver temperature. The half-power beamwidth (HPBW) of the telescope is \sim 14" and the main-beam efficiency, η_{mb} , is 0.63. Data were obtained in the position-switching mode with offset 20 west

in azimuth. Pointing and focus was checked regularly at a 2-hour interval. The resultant spectra are on the antenna temperature scale, T_A^* , which has been corrected from chopper wheels calibration for atmospheric transmission and losses associated with rearward scattering. Since the spatial extent of each emission source is not known, no main beam correction is applied. Further corrections for the forward scattering and spillover efficiency ($\eta_{fss}=0.82$) convert the source antenna temperature, T_A^* , to the source brightness temperature, T_R^* .

By employing the Dutch Autocorrelation Spectrometer (DAS) backend with two subsystems and a bandwidth of 500 MHz for dual-polarity operation, we have a spectral resolution of 756 kHz and a channel spacing of 625 kHz. Typically an integration time of 3 to 4 hours was achieved. Velocity shifting of $\pm 4.5~{\rm km~s^{-1}}$ with respect to the nominal LSR velocity, about $\pm 5~{\rm MHz}$ with respect to the rest frequency in the 345 GHz band, was executed as a common practice during observations in order to neutralize the effect of possible low-level gain variations in the DAS and to identify potential interlopers from the image sideband. The JCMT data were reduced using the SPECX spectral line reduction package.

Observations of submillimeter high-frequency transitions yield smaller telescope beams, preferentially sample the warmer and denser regions, and help to avoid line confusion with interloping emission from cooler envelope material along the line-of-sight. At hot core temperatures of 100 K or more, searches in the submillimeter regime are further favoured by the fact that the higher frequency transitions are expected to be intrinsically stronger.

Good agreement between observed line frequencies and those measured in the laboratory, for four or more spectral lines, are the minimum requirements for claiming identification of a new interstellar molecule. The rotational spectrum of pyrimidine has recently been measured over the spectral range 3-337 GHz, and the calculated dipole moment of pyrimidine is $\mu_{tot} = \mu_b = 2.39$ Debye (Kisiel et al. 1999). Hence only b-type transitions are observable. Our astronomical search was based on the best candidate transitions of pyrimidine in spectral regions free from known spectral line contamination. Four bandheads made up of closely spaced high-J transitions (at higher energy levels) plus 2 pairs of low-J doublet lines were observed in a total of 6 different spectral bands. The observed transitions are listed in Table 2; transitions with line strengths smaller than 10.0 are not included. Column 1 lists the line number; each line may include multiple pyrimidine transitions which are blended into one unresolved, single spectral-line feature.

Figure 1 illustrates the predicted relative line intensity in an arbitrary scale of the pyrimidine spectra over a frequency range of 0 to 500 GHz at various rotational temperatures ($T_{rot}=50$ K, the top panel; 100 K, the middle panel; and 200 K, the bottom panel). All possible spectral blends are accounted for in the simulation, which is made for a Gaussian lineshape with an assumed equivalent linewidth (FWHM) of 7 km s⁻¹. Note that the linewidth, when Doppler converted from velocity to frequency, increases with frequency, which is conducive to the formation of stronger blends at higher frequencies.

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Table 2. Pyrimidine transitions observed.

Table 2. (continued).

	v				-				
Line	Rest Frequency	Transition	S_{ul}^{\star}	$\mathrm{E}_{\mathrm{l}}^{\dagger}$	Line	Rest Frequency	Transition	S_{ul}^{\star}	$\mathrm{E}_{\mathrm{l}}^{\dagger}$
	(MHz)	$J_{K_a,K_c}-J_{K_a^\prime,K_c^\prime}$		(cm^{-1})		(MHz)	$J_{K_a,K_c}-J_{K_a^\prime,K_c^\prime}$		(cm^{-1})
	220061 004	F2 F2	E9 49	200 07		242220 002	EF FA	E 1 10	211.00
1	329961.004	$53_{1,53} - 52_{0,52}$	52.48	288.87	4	342289.902	$55_{1,55} - 54_{0,54}$	54.48	311.09
	329961.004	$53_{0,53} - 52_{1,52}$	52.48	288.87		342289.902	$55_{0,55} - 54_{1,54}$	54.48	311.09
	329963.042	$52_{2,51} - 51_{1,50}$	50.45	288.46		342290.286	$44_{12,33} - 43_{11,32}$	32.80	283.93
	329963.042	$52_{1,51} - 51_{2,50}$	50.45	288.46		342290.286	$44_{11,33} - 43_{12,32}$	32.80	283.93
	329963.507	$43_{11,33} - 42_{10,32}$	32.73	266.24		342290.410	$43_{12,31} - 42_{13,30}$	30.91	278.99
	329963.507	$43_{10,33} - 42_{11,32}$	32.73	266.24		342290.410	$43_{13,31} - 42_{12,30}$	30.91	278.99
	329963.584	$42_{12,31} - 41_{11,30}$	30.83	261.71		342290.681	$45_{10,35} - 44_{11,34}$	34.70	288.46
	329963.584	$42_{11,31} - 41_{12,30}$	30.83	261.71		342290.681	$45_{11,35} - 44_{10,34}$	34.70	288.46
	329963.825	$44_{10,35} - 43_{9,34}$	34.65	270.36		342291.342	$42_{13,29} - 41_{14,28}$	29.03	273.64
	329963.825	$44_{9,35} - 43_{10,34}$	34.65	270.36		342291.342	$42_{14,29} - 41_{13,28}$	29.03	273.64
	329964.312	$41_{12,29} - 40_{13,28}$	28.95	256.77		342291.379	$46_{9,37} - 45_{10,36}$	36.62	292.58
	329964.312	$41_{13,29} - 40_{12,28}$	28.95	256.77		342291.379	$46_{10,37} - 45_{9,36}$	36.62	292.58
	329964.345	$45_{9,37} - 44_{8,36}$	36.58	274.06		342291.921	$54_{1,53} - 53_{2,52}$	52.45	310.68
	329964.345	$45_{8,37} - 44_{9,36}$	36.58	274.06		342291.921	$54_{2,53} - 53_{1,52}$	52.45	310.68
	329964.448	$51_{3,49} - 50_{2,48}$	48.43	287.64		342292.209	$47_{8,39} - 46_{9,38}$	38.56	296.28
	329964.448	$51_{2,49} - 50_{3,48}$	48.43	287.64		342292.209	$47_{9,39} - 46_{8,38}$	38.56	296.28
	329964.911	$46_{8,39} - 45_{7,38}$	38.52	277.36		342293.032	$48_{8,41} - 47_{7,40}$	40.51	299.58
	329964.911	467,39 - 458,38	38.52	277.36		342293.032	487,41 - 478,40	40.51	299.58
	329965.303	$50_{3,47} - 49_{4,46}$	46.43	286.41		342293.280	$53_{3,51} - 52_{2,50}$	50.43	309.86
	329965.303	$50_{4,47} - 49_{3,46}$	46.43	286.41		342293.280	$53_{2,51} - 52_{3,50}$	50.43	309.86
	329965.396	$47_{7,41} - 46_{6,40}$	40.48	280.24		342293.488	$41_{14,27} - 40_{15,26}$	27.17	267.87
	329965.396	$47_{6,41} - 46_{7,40}$	40.48	280.24		342293.488	$41_{15,27} - 40_{14,26}$	27.17	267.87
	329965.687	$49_{4,45} - 48_{5,44}$	44.43	284.76		342293.729	$49_{6,43} - 48_{7,42}$	42.47	302.46
	329965.687	$49_{5,45} - 48_{4,44}$	44.43	284.76		342293.729	$49_{7,43} - 48_{6,42}$	42.47	302.46
	329965.688	$48_{6,43} - 47_{5,42}$	42.45	282.71		342294.057	$52_{3,49} - 51_{4,48}$	48.43	308.63
	329965.688	$48_{5,43} - 47_{6,42}$	42.45	282.71		342294.057	$52_{4,49} - 51_{3,48}$	48.43	308.63
	329966.047	$40_{14,27} - 39_{13,26}$	27.08	251.42		342294.195	$50_{5,45} - 49_{6,44}$	44.44	304.93
	329966.047	$40_{13,27} - 39_{14,26}$	27.08	251.42		342294.195	$50_{6,45} - 49_{5,44}$	44.44	304.93
	020000.011	1013,27 0014,26	21.00	201.12		342294.334	$51_{5,47} - 50_{4,46}$	46.43	306.98
2	336125.535	$54_{1,54} - 53_{0,53}$	53.48	299.88		342294.334	$51_{5,47} - 50_{5,46}$	46.43	306.98
-	336125.535	$54_{0,54} - 53_{1,53}$	53.48	299.88		342297.447	$40_{15,25} - 39_{16,24}$	25.33	261.70
	336127.005	$43_{12,32} - 42_{11,31}$	31.81	272.72		342297.447	$40_{15,25} - 39_{15,24}$ $40_{16,25} - 39_{15,24}$	25.33	261.70
	336127.005	$43_{12,32} - 42_{11,31}$ $43_{11,32} - 42_{12,31}$	31.81	272.72		042231.441	4016,25 - 3315,24	20.00	201.70
				277.25	5	249452 267	44.000 42.00	21.90	200 41
	336127.169	$44_{10,34} - 43_{11,33}$	33.72		5	348453.267	$44_{12,32} - 43_{13,31}$	31.89	290.41
	336127.169	$44_{11,34} - 43_{10,33}$	33.72	277.25		348453.267	$44_{13,32} - 43_{12,31}$	31.89	290.41
	336127.422	$42_{12,30} - 41_{13,29}$	29.92	267.78		348453.422	$45_{12,34} - 44_{11,33}$	33.78	295.35
	336127.422	$42_{13,30} - 41_{12,29}$	29.92	267.78		348453.422	$45_{11,34} - 44_{12,33}$	33.78	295.35
	336127.563	$53_{2,52} - 52_{1,51}$	51.45	299.47		348453.838	$43_{14,30} - 42_{13,29}$	30.01	285.06
	336127.563	$53_{1,52} - 52_{2,51}$	51.45	299.47		348453.838	$43_{13,30} - 42_{14,29}$	30.01	285.06
	336127.680	$45_{10,36} - 44_{9,35}$	35.63	281.37		348454.040	$46_{11,36} - 45_{10,35}$	35.69	299.88
	336127.680	$45_{9,36} - 44_{10,35}$	35.63	281.37		348454.040	$46_{10,36} - 45_{11,35}$	35.69	299.88
	336128.356	$46_{8,38} - 45_{9,37}$	37.57	285.07		348454.101	$56_{1,56} - 55_{0,55}$	55.48	322.51
	336128.356	469,38 - 458,37	37.57	285.07		348454.101	$56_{0,56} - 55_{1,55}$	55.48	322.51
	336128.740	$41_{14,28} - 40_{13,27}$	28.05	262.43		348454.919	$47_{10,38} - 46_{9,37}$	37.61	304.00
	336128.740	$41_{13,28} - 40_{14,27}$	28.05	262.43		348454.919	$47_{9,38} - 46_{10,37}$	37.61	304.00
	336128.946	$52_{3,50} - 51_{2,49}$	49.43	298.65		348455.498	$42_{14,28} - 41_{15,27}$	28.15	279.29
	336128.946	$52_{2,50} - 51_{3,49}$	49.43	298.65		348455.498	$42_{15,28} - 41_{14,27}$	28.15	279.29
	336129.052	$47_{8,40} - 46_{7,39}$	39.51	288.36		348455.899	$48_{9,40} - 47_{8,39}$	39.55	307.70
	336129.052	$47_{7,40} - 46_{8,39}$	39.51	288.36		348455.899	$48_{8,40} - 47_{9,39}$	39.55	307.70
	336129.643	$48_{6,42} - 47_{7,41}$	41.47	291.24		348456.112	$55_{2,54} - 54_{1,53}$	53.45	322.10
	336129.643	$48_{7,42} - 47_{6,41}$	41.47	291.24		348456.112	$55_{1.54} - 54_{2.53}$	53.45	322.10
	336129.762	$51_{3,48} - 50_{4,47}$	47.43	297.42		348456.848	$49_{8,42} - 48_{7,41}$	41.50	310.99
	336129.762	$51_{4,48} - 50_{3,47}$	47.43	297.42		348456.848	$49_{7,42} - 48_{8,41}$	41.50	310.99
	336130.023	$49_{6,44} - 48_{5,43}$	43.45	293.71		348457.447	$54_{2,52} - 53_{3,51}$	51.43	321.28
	336130.023	$49_{5,44} - 48_{6,43}$	43.45	293.71		348457.447	$54_{3,52} - 53_{2,51}$	51.43	321.28
	336130.092	$50_{5,46} - 49_{4,45}$	45.43	295.77		348457.650	$50_{6,44} - 49_{7,43}$	43.47	313.87
	336130.092	$50_{5,46} - 49_{5,45}$ $50_{4,46} - 49_{5,45}$	45.43	295.77		348457.650	$50_{6,44} - 49_{7,43}$ $50_{7,44} - 49_{6,43}$	43.47	313.87
	336131.417	$40_{15,26} - 39_{14,25}$	26.20	256.66		348458.186	$50_{7,44} - 49_{6,43}$ $53_{3,50} - 52_{4,49}$	49.42	320.04
			26.20 26.20				, ,		
	336131.417	$40_{14,26} - 39_{15,25}$	∠0. <i>∠</i> 0	256.66		348458.186	$53_{4,50} - 52_{3,49}$	49.42	320.04
9	990017 010	97 90	94.07	146.00		348458.202	$51_{5,46} - 50_{6,45}$	45.44	316.34
3	338017.612	$27_{27,1} - 26_{26,0}$	24.97	146.26		348458.202	$51_{6,46} - 50_{5,45}$	45.44	316.34
	338018.346	$27_{27,0} - 26_{26,1}$	24.97	146.26		348458.410	524,48 - 515,47	47.43	318.40
						348458.410	$52_{5,48} - 51_{4,47}$	47.43	318.40

Table 2. (continued).

Line	Rest Frequency (MHz)	$\begin{array}{c} {\rm Transition} \\ {\rm J_{K_a,K_c} - J_{K_a',K_c'}} \end{array}$	S_{ul}^{\star}	$\begin{array}{c} E_l^{\dagger} \\ (cm^{-1}) \end{array}$
	348458.771 348458.771	$41_{15,26} - 40_{16,25} 41_{16,26} - 40_{15,25}$	26.30 26.30	273.12 273.12
6	363098.770 363099.057	$\begin{array}{c} 29_{29,1} - 28_{28,0} \\ 29_{29,0} - 28_{28,1} \end{array}$	26.97 26.97	169.23 169.23

- * Line Strength.
- † Lower energy level.

The strongest lines arise from blends of many transitions in high-J bandheads. These bandheads become more compact and have more lines at higher frequencies. On the other hand, following Boltzmann population distribution, intensities of individual transitions forming the spectral blends, or bands, maximize at appreciably lower frequencies (henceforth the Boltzmann maxima) than the maxima apparent in the spectral profiles in Figure 1. At $T_{rot} = 100$ K, for example, the strongest individual band line, i.e., the Boltzmann maximum, though not obvious in the spectrum (the middle panel of Figure 1), is near 195 GHz. Nevertheless, because at such frequencies the band compression effect becomes dominant and compensates for the intensity decrease of transitions at frequencies beyond the Boltzmann maximum, the overall band profile reaches an intensity maximum at the much higher frequency of ~ 300 GHz. Similarly at $T_{rot} = 50$ K and 200K, the Boltzmann maxima are at \sim 135 GHz and \sim 285 GHz, respectively, while at higher frequencies where band compression dominates, the apparent maximum intensity features for a linewidth of 7 km s^{-1} are predicted to be at ~ 180 GHz and ~ 335 GHz, accordingly. The 324 GHz spectral blend, which protrudes above the general profile and is seen in the middle and bottom panels of Figure 1, arises from accidental addition of some non-band lines to the spectral blend. The prevailing spectral features at 100 K and 200 K are compact high-J R-type bandheads of the type observed in our search (see Table 2). For an excitation temperature near 100 K, it is clear that searches in the spectral region near 1-mm (300 GHz) should provide the best chance for a detection.

3 RESULTS

Table 3 lists the important measured physical parameters of all the pyrimidine lines observed. The pyrimidine lines are separated into three sources according to the actual observations (Column 1). Column 2 gives the line numbers, which correspond to the line numbers shown in Column 1 of Table 2. Most of the pyrimidine lines are only observed in one or two sources but not in all. The fact that most of the data are fragmentary is mainly due to scheduling difficulties at the JCMT, leading to limited or uncertain availability of observing time for different sources.

In total, 6 different pyrimidine lines were observed toward the 3 target sources. The peak antenna temperature of the spectral line observed, i.e. the T_A^* upper limit for a non-dection, is given in Column 3 in mK; "rms" indicates the 1- σ noise level per channel of the spectrum, where $\sigma \equiv T_A^*(rms)$.

Column 4 lists the upper limits of the total column density N_{tot} derived. T_A^* , hence also N_{tot} , are not listed if the target pyrimidine line is completely overwhelmed by nearby strong interlopers. Self-explanatory comments for each spectral line observed in each source are given, when necessary, in Column 5. Interlopers, which are largely blended with (denoted as "(B)") and smeared out the target pyrimidine lines or partially blended (denoted as "(PB)") with the candidate lines, are also included in Column 5 in the format molecule/frequency(MHz).

Assuming that the pyrimidine lines are optically thin, in LTE, and that the rotational excitation temperature, T_{rot} , is much higher than the background brightness temperature, the beam-averaged total column density of c-C₄H₄N₂ can be written as:

$$N_{tot}(\text{cm}^{-2}) = (1.669 \times 10^{17}) \frac{W_K Q_{rot}}{\nu} \left\{ \sum \left[\frac{S_{ul} \ \mu_b^2}{\exp\left(\frac{E_u}{T_{rot}}\right)} \right] \right\}^{-1}, (1)$$

where

$$W_K = \int {\rm T_R}^* dv = \int \frac{{\rm T_A}^*}{\eta_{fss}} dv \tag{2}$$

in (K km s⁻¹) is the integrated intensity of the spectral line either from a single pyrimidine transition, or from unresolved multi-transitions such as in a bandhead. The rest frequency (MHz) is ν , μ_b the permanent b-dipole moment in Debye, S_{ul} the line strength, E_u the upper energy level in K and Q_{rot} the rotational partition function. All pyrimidine lines reported here contain more than one pyrimidine transition, a summation of $(S_{ul}\mu_b^2)/[\exp(E_u/T_{rot})]$ over all relevant transitions was thus applied. In addition, a rotational temperature $T_{rot} = 100 \text{ K}$ was assumed for all transitions. In the case of a non-detection, for an interloper-blended pyrimidine line, T_R^* is obtained from the T_A^* upper limit listed in Column 3 of Table 3 corrected for η_{fss} . If the equivalent linewidth could not be unambiguously defined from the observed spectrum, the column density limits were evaluated using a representative value of the equivalent linewidth; a value of $\Delta v \simeq 10 \text{ km s}^{-1}$ was adopted for all three target sources.

Sample pyrimidine spectra are shown in Figures 2 and 3. With a limited number of spectral lines observed in each source, our submillimeter-wave search for pyrimidine did not yield a definite detection of pyrimidine in either Sgr B2(N) or Orion KL. By averaging over all observed lines measurable in each source (see Table 3), the inferred upper limits on the total column density in Sgr B2 and Orion are 1.7×10^{14} cm⁻² and 2.4×10^{14} cm⁻², respectively.

In the case of W51 e1/e2, there is a spectral feature at $\sim 57~\rm km~s^{-1}$ with respect to the rest frequency adopted for the observation (see the spectrum shown in the lower panel of Figure 3). This feature coincides precisely with the J \leq 55 band-head of pyrimidine between 342289.9 and 342297.4 MHz (Line 4), containing 32 transitions at $\rm V_{LSR}=59.0~km~s^{-1}$. An unidentified U-line at 342290.0 MHz was previously reported in a line survey of Orion KL (Schilke, et al. 1997); unfortunately we did not observe either Orion or Sgr B2 at this particular frequency.

The total pyrimidine column density in W51 e1/e2 derived solely from Line 4 is 4.8×10^{14} cm⁻²; the averaged upper limit to the column density from all 3 lines available in

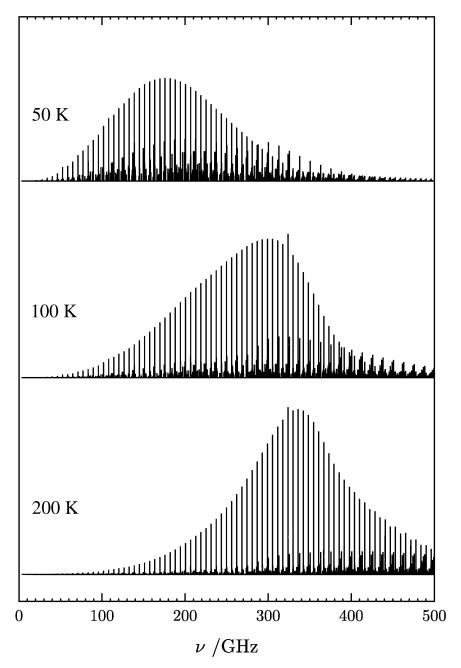


Figure 1. The predicted relative line intensity of the pyrimidine spectra over a frequency range of 0 to 500 GHz at various excitation temperatures (50 K, top; 100 K, middle; and 200 K, bottom). The ordinate is in an arbitrary scale. These spectra are actually contour plots with point spacing of 0.5 MHz but have the appearance of stick diagrams because line contours are very narrow relative to the total breadth of the plotted spectrum. Each such stick is thus in fact a very compressed line profile for a spectral blend, and each spectrum is in principle 1000000 points long. The simulation is for a Gaussian lineshape with an assumed equivalent linewidth (FWHM) of 7 km s⁻¹. The apparent maximum intensity features are at \sim 180 GHz for 50 K, \sim 300 GHz for 100 K and \sim 335 GHz for 200 K. The 324 GHz spectral peak (middle & bottom) is due to accidental addition of some non-band lines to the spectral blend.

W51 is $N_{tot} \leq 3.4 \times 10^{14}$ cm⁻². It is interesting to note that the pyrimidine column density computed only from Line 4 (assuming $T_{rot} = 100$ K) is just slightly higher (within a factor of 2) than the upper limits deduced from the two other, interloper-contaminated, lines. It appears that if Line 4 of W51 is truly a detection, we may have expected to detect another bandhead, Line 5, whose transitions are at higher frequencies. It could be argued that the fact that we failed to detect Line 5 makes the identification of Line 4 less likely.

However, Line 5 is expected to be much weaker than Line 4 at an excitation temperature lower than $100~\mathrm{K}$, and so, in the absence of accurately measured pyrimidine rotational temperatures for these sources, we cannot entirely rule out a true detection in W51.

Finally, the submillimeter transitions targeted in this search possess rather high excitation levels, and so any observable pyrimidine emission would mostly originate from regions of high temperature and/or density, if radiative ex-

W51 e1/e2

W51 e1/e2

Source	Line	$T_A^* \pm rms \pmod{mK}$	N_{tot} $(10^{14} \text{ cm}^{-2})$	Comment
Sgr B2(N)	1			(B) $C_2H_5OH/329954.9$; (B) $C_2H_5OH/329956.5$; (B) $C_2H_5OH/329968.2$
Sgr B2(N)	3	52.6 ± 13.5	< 1.68	(B) CH ₃ OCH ₃ /338025.5
Sgr B2(N)	5			(B) $CH_3CHO/348449.6$; (B) $C_2H_5CN/348473$
Orion KL	2	215.7 ± 13.8	<1.18	(B) c-C ₃ H ₂ /336128.5; (B) C ₂ H ₃ CN/336137.8; (PB) HCOOCH ₃ /336111.3; (PB) SO ₂ /336113.5
Orion KL	5	400.0 ± 12.6	< 3.66	contaminated by a spectral feature from the image sideband
Orion KL	6			(B) $CH_3C_3N/363097.1$; (B) $Si^{18}O/363100.7$; (B) $C_2H_5CN/363107$
W51 e1/e2	3	140.6 ± 12.9	< 3.14	(B) CH ₃ OCH ₃ /338025.5

(B) CH₃CHO/348449.6

detected? (U-342290); (PB) C₂H₃CN/342286.8

Table 3. The measured physical parameters of the pyrimidine lines observed.

< 4.79

< 2.20

citation is negligible. As a result, these excited pyrimidine molecules would have been located in regions fairly close to protostellar hot cores within molecular clouds. It is therefore probable that the real source size is smaller than the telescope beam (${\sim}14^{''}$); it is more likely to be the case particularly for distant sources such as Sgr B2(N) and W51 e1/e2. Hence, one should note that our observations would suffer from beam dilution if the source extent is indeed smaller than the beam. The derived upper limits on the column densities, based on the assumption that the source fills the beam, could consequently be underestimated.

 631.3 ± 23.6

 127.5 ± 12.3

The upper limits of fractional abundance of pyrimidine with respect to molecular hydrogen, $X(c-C_4H_4N_2)=N_{tot}(c-C_4H_4N_2)/N_{tot}(H_2)$, may also be deduced. Molecular hydrogen column densities inferred from single-dish observations with beam sizes similar to the JCMT are employed, in order to determine the beam-averaged abundances more accurately. The H₂ column densities adopted are: $\simeq 5\times 10^{24}~{\rm cm}^{-2}$ for Sgr B2(N) (Nummelin et al. 2000), $8\times 10^{23}~{\rm cm}^{-2}$ for Orion KL (Sutton et al. 1995), and $1\times 10^{24}~{\rm cm}^{-2}$ for W51 e1/e2 (Jaffe, Becklin & Hildebrand 1984). The upper limits of pyrimidine fractional abundances thus estimated are $X(c-C_4H_4N_2)\leqslant 3.4\times 10^{-11}$ for Sgr B2, 3.0 $\times 10^{-10}$ for Orion, and 3.4×10^{-10} for W51.

4 DISCUSSION

Our submillimeter search for the nucleic acid building-block pyrimidine has not been successful. We have perhaps detected one-line in a single source but this needs to be confirmed. The negative result therefore cannot be considered definitive and searches at lower frequencies may yet detect pyrimidine in hot cores. The low inferred pyrimidine abundance limits may simply reflect the fact that pyrimidine is generally of low abundance in massive star-forming cores, and hence it is difficult to populate the high-J energy levels (J \leqslant 56 in our study) which are observable at submillimeter wavelengths. On the other hand, it could also imply that either pyrimidine is not evaporated efficiently from dust grains at hot core temperatures, or is destroyed easily in the warmest regions in hot cores sampled by submillimeter observations.

It would appear that the best chance for an astronom-

ical detection of pyrimidine, and other Nitrogen Heterocycles, is probably in the circumstellar envelopes (CSEs) of carbon stars. AGB and post-AGB stars (e.g. IRC+10216, CRL 618 and CRL 2688) are copious producers of carbonaceous dust particles. Recent ISO observations of well-known protoplanetary nebulae (PPNe) have uncovered more new organic molecules, including the first detection of benzene in CRL 618 (Cernicharo et al. 2001a, 2001b). The initial stages of dust formation involve polymerization of acetylene to form benzene and subsequent C₂H₂ additions lead to large polycyclic aromatic hydrocarbon (PAH) molecules (e.g. Cherchneff, Barker & Tielens 1992). During this reaction sequence other triply-bonded molecules can also add to the growing ring structures. In particular, recent theoretical work indicates that N atoms can become incorporated in ring structures through additions involving HCN (Ricci, Bauschlicher & Bakes 2001). However, the kinetics of ring growth suggests that single rings containing two N atoms will be less favoured than single rings with one N atom (i.e. pyridine). Even two-ring compounds containing a single N atom, such as quinoline and isoquinoline, the Nsubstituted analogues of naphthalene, could be more abundant than pyrimidine (Kisiel et al. 2003) and may explain why our search appears to have been unsuccessful. Searches for pyridine, quinoline and isoquinoline in the molecular envelopes of evolved stars are currently underway.

As an alternative to ring formation in neutral-neutral reactions, Woods, et al. (2002) have shown that ion-molecule reactions are able to account for the abundance of benzene observed in CRL 618. The growth of larger rings, and incorporation of heteroatoms into them, has not yet been considered in circumstellar ion-molecule chemistry. Woods, et al. (2003) have proposed one neutral process, involving benzene and CN, that could lead to nitrogen being added to ring structures. However, the product of this reaction has the nitrogen present in a side-group (i.e. benzonitrile, $c\text{-}\mathrm{C}_6\mathrm{H}_5\mathrm{CN}$) and not bonded into the ring.

Another possible reason for a low interstellar pyrimidine abundance concerns its photostability. The infrared spectra and photostability of pyrimidine have recently been measured in an Ar matrix at 10 K (Peeter et al. 2003). The stability of pyrimidine (which does not have real aromatic properties) against UV photolysis is rather limited and far below that of mono and polycyclic aromatic rings. These ex-

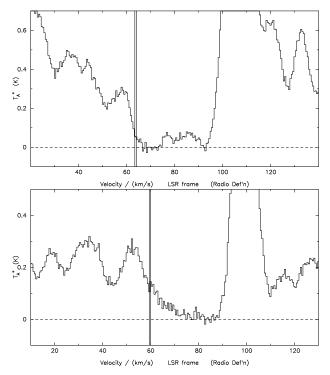


Figure 2. Sample pyrimidine spectra at 338.0 GHz (Line 3; $27_{27,1}$ - $26_{26,0}$ and $27_{27,0}$ - $26_{26,1}$) of Sgr B2(N) (top) and of W51 e1/e2 (bottom). The two vertical lines mark the two expected transitions of pyrimidine. The abscissae give the LSR velocities with respect to the rest frequencies adopted for the observations at the nominal LSR velocities 64.0 km s⁻¹ for Sgr B2(N) and 60.0 km s⁻¹ for W51 e1/e2.

periments appear to indicate that any circumstellar pyrimidine would be easily destroyed by UV photons, or cosmic ray particles, soon after delivery to the interstellar medium. In this case, any interstellar pyrimidine would have to be produced in dark molecular clouds.

5 CONCLUSION

To strengthen the role of prebiotic interstellar matter in Astrobiology, we have searched for 6 pyrimidine lines in three massive star-forming regions: Sgr B2(N), Orion KL and W51 e1/e2. Our search was unsuccessful and did not yield a conclusive result, with only one potential single-line detection. The abundance limits inferred are $\leq 3.4 \times 10^{-11}$ for Sgr B2, 3.0×10^{-10} for Orion, and 3.4×10^{-10} for W51. Our negative result may simply reflect the fact that interstellar pyrimidine is of low abundance. Sources that are ongoing sites of carbon dust formation, such as the C-rich envelopes of AGB and post-AGB stars, probably present the best opportunity for detecting pyrimidine and other nitrogen heterocycles.

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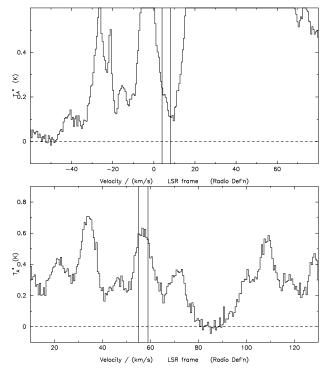


Figure 3. Sample pyrimidine spectra at the 336.1 GHz band head (Line 2; with $J \le 54$) of Orion KL (top), and at the 342.3 GHz band head (Line 4; with $J \le 55$) of W51 e1/e2 (bottom). The two verticals enclose the 336.1 GHz band head (top) and the 342 GHz band head (bottom). A *tentative* detection of pyrimidine in W51 e1/e2 is visible in the bottom panel. The assumed LSR velocities for the rest frequencies adopted for the observations are 8.0 and 60.0 km s⁻¹ for Orion KL and W51 e1/e2, respectively.

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